Simultaneous Binding of Betaine and Pseudohalide to Cadmium: Structures of Four Polymeric Mixed-ligand Cadmium(II) Complexes[†]

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Four cadmium complexes containing betaine and pseudohalide ligands have been synthesised and structurally characterized by single-crystal X-ray analysis. The betaine–azide complex $[Cd_2(Me_3NCH_2CO_2)_2(N_3)_4]$ **1** and the betaine–isocyanate $[Cd_2(Me_3NCH_2CO_2)_2(NCO)_4]$ **2** are isomorphous, crystallizing in the monoclinic space group *C*2/*c* with *Z* = 4. The two betaine–thiocyanate complexes $[Cd_3(Me_3NCH_2CO_2)_4(SCN)_6(H_2O)_2]$ **3** and $[Cd(Me_3NCH_2CH_2CO_2)(NCS)_2]$ **4** are both triclinic, space group $P\bar{1}$ with *Z* = 1 and 2, respectively. All four complexes are polymeric, the carboxy groups of the betaine ligands acting in three co-ordination modes and the pseudohalide ligands in two typical bridging modes. The structure of **1** or **2** consists of a virtually linear chain in which each pair of adjacent metal ions are triply bridged by one carboxylate plus two μ-1,1-pseudohalogenide ligands. The framework of **3** is a one-dimensional chain built from corner-sharing centrosymmetric 16-membered $(\text{-N-C-S-Cd})_4$ puckered rings containing μ-1,3-bridging thiocyanate groups in both *anti* and skew modes; both uni- and bi-dentate chelating modes of the betaine ligands coexist in this complex. The structure of **4** is constructed from an alternate arrangement of two kinds of rings which share corners to form a linear chain: one is an eight-membered chair-like $(\text{-N-C-S-Cd})_2$ ring bridged by a pair of μ-1,3-thiocyanate ligands and the other a four-membered $(\text{-O-Cd})_2$ ring bridged by two carboxylate ligands. The significance of these structural features and the co-ordination geometries at the cadmium centres are discussed.

Betaine, *i.e.* trimethylammonioacetate ($Me_3N^+CH_2CO_2^-$, L^1) also known as lycine,[1] is a biological base and a methyl-transfer agent in amino acid synthesis[2,3] and also widely distributed in plants and animals. It and its derivative trimethylammoniopropionate ($Me_3N^+CH_2CH_2CO_2^-$, L^2) can be considered as amino acid derivatives, especially in regard to their co-ordination behaviour. Amino acids such as proline[4] and its derivatives[5] commonly act as zwitterionic species in ligation with metal centres. Likewise betaine, as well as its analogues, existing solely in the zwitterionic form, is found to co-ordinate metal centres in different molar ratios *via* its carboxylate moiety.[6-14]

In the past several decades metal pseudohalide complexes have been extensively studied with incorporation of neutral nitrogen-donor ligands such as pyridine derivatives[15-19] and polyamines.[20-23] In view of the negative charge that accompanies the binding of pseudohalides to a metal ion, it is difficult to attach one or more anionic carboxylate groups to form a metal carboxylate pseudohalide system. Mixed-ligand complexes of this type may conceivably be achieved by using neutral zwitterionic ligands containing carboxy oxygen donors such as amino acids and betaine derivatives instead of anionic carboxylates.

Although several cadmium(II) complexes containing zwitterionic carboxylate ligands such as amino acids,[4,5] betaine and its derivatives[24,25] have been reported, much less is known concerning the concerted binding of zwitterionic carboxylate groups and pseudohalides to Cd^{II}. The versatile binding modes of carboxylates and pseudohalides such as chelating and bridging to metal centres are expected to lead to an enrichment of structural varieties including oligo- or poly-meric complexes. We have now isolated a series of complexes in the cadmium–betaine–pseudohalide system and succeeded in obtaining their crystalline forms. The crystal structures of $[Cd_2L^1_2(N_3)_4]$ **1**, $[Cd_2L^1_2(NCO)_4]$ **2**, $[Cd_3L^1_4(SCN)_6(H_2O)_2]$ **3** and $[CdL^2(NCS)_2]$ **4** have been determined in order to establish the binding of betaines to Cd^{II} with concomitant co-ordination of pseudohalide, as well as to differentiate betaine and its derivatives from the typical carboxylic acids in regard to their ligand properties. To our knowledge, **4** is the first example of a cadmium(II) complex exhibiting simultaneous bidentate chelate and monatomic bridge modes of co-ordination by a carboxylate-like betaine ligand.

Experimental

Materials and Measurements.—Sodium azide, sodium cyanate and potassium thiocyanate were obtained from E. Merck. Cadmium(II) nitrate tetrahydrate and anhydrous trimethylammonioacetate were from Riedel-de Haën and Sigma, respectively. The compound L^2 was synthesised by the reaction of 3-bromopropanoic acid with trimethylamine.[10] The densities of the crystals were measured by flotation in CCl_4–1,2-dibromoethane. Infrared spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet 205 FTIR spectrometer. The presence of cadmium in the crystals was initially determined using a Spectrace 5000 Tracor X-ray fluorometer.

CAUTION: Heavy-metal azides are potentially explosive. Only small amounts should be prepared and handled with great caution; heating must be avoided. The attempted preparation of a mercury(II)–betaine–azide complex resulted in an explosion during slow evaporation of the solvent.

Preparation of Compounds.—$[Cd_2L^1_2(N_3)_4]$ **1**. To cadmium(II) nitrate tetrahydrate (200 mg, 0.65 mmol) dissolved in distilled water (10 cm^3) was added L^1 (300 mg, 2.60 mmol) dissolved in the minimum amount of water. Dropwise addition of aqueous sodium azide (50 mg, 0.77 mmol) solution (1 cm^3) immediately gave a white precipitate. After the precipitate was

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[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

filtered off, the filtrate was allowed to stand for several hours. Colourless prismatic crystals of **1** were obtained.

$[Cd_2L^1{}_2(NCO)_4]$ **2**. This compound was synthesised by the above procedure with a cadmium : L^1 : cyanate molar ratio of 1 : 2 : 1. Slow evaporation at room temperature yielded colourless polyhedral crystals of **2**, which were collected and air-dried.

$[Cd_3L^1{}_4(SCN)_6(H_2O)_2]$ **3**. A solution containing $Cd(NO_3)_2 \cdot 4H_2O$ (225 mg, 0.73 mmol) and anhydrous L^1 (170 mg, 1.50 mmol) was prepared in warm absolute methanol (20 cm^3). A methanolic solution (3 cm^3) of potassium thiocyanate (140 mg, 1.40 mmol) was added dropwise with slight shaking. The resulting colourless solution was allowed to stand for several days at room temperature, and colourless polyhedral crystals of **3** were deposited. They were filtered off and air dried.

$[CdL^2(NCS)_2]$ **4**. A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (220 mg, 0.71 mmol) and L^2 (230 mg, 1.75 mmol) was dissolved in absolute methanol (15 cm^3). It was stirred and methanolic potassium thiocyanate (3 cm^3; 100 mg, 1.03 mmol) added dropwise. The resulting solution became cloudy after complete addition. It was then filtered and the clear filtrate allowed to evaporate slowly. Crystallization began after several days, and colourless polyhedral crystals of **4** were collected and air-dried.

Crystallographic Data Collection and Structure Determination.—Information concerning crystallographic data collection and structure refinement is summarized in Table 1. Data collection was preformed in the ω-scan mode[26] on a Nicolet R3m/V diffractometer using Mo-Kα radiation ($\lambda = 0.710\,73$ Å) at 293 K. Unit-cell parameters were calculated from least-squares fitting of the 2θ angles for 25 selected strong reflections. Crystal stability was monitored by recording two check reflections at intervals of 125 data measurements, and no significant variation was detected. The intensity data were processed with a learnt-profile procedure,[27] and an empirical absorption correction based on ψ-scan data were also applied.

The cadmium atoms in all structures were located by the Patterson method and the remaining non-hydrogen atoms were derived from subsequent Fourier difference syntheses. All non-hydrogen atoms were refined anisotropically by full-matrix least squares. The hydrogen atoms of the betaine ligands were placed in calculated positions with C–H 0.96 Å, assigned fixed isotropic thermal parameters, and allowed to ride on their respective parent carbon atoms.

All calculations were carried out on a DEC MicroVAX-II computer using the SHELXTL-PLUS program package.[29] Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[30] Final atomic coordinates for the four crystal structures, along with their estimated standard deviations, are presented in Tables 2–4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

Description of the Structures.—$[Cd_2L^1{}_2(N_3)_4]$ **1** *and* $[Cd_2L^1{}_2(NCO)_4]$ **2**. Complexes **1** and **2** are isomorphous, having the same basic skeleton and differing only in the pseudohalide ligands; bond lengths and angles are given in Table 5. Their structures are very similar to those of dichloro(4-hydroxy-L-proline)cadmium(II), $[Cd(Hhpro)Cl_2]$,[5] and dichloro(proline)cadmium(II) hydrate, $[Cd(Hpro)Cl_2] \cdot H_2O$.[4] In addition to complex **1**, the isomorphous complexes $[Co_2L^1{}_2(N_3)_4]$ and $[Zn_2L^1{}_2(N_3)_4]$ have also been prepared in the same way[31] using cobalt(II) nitrate and zinc(II) sulfate, respectively, instead of cadmium(II) nitrate. In all of the above complexes the amino acids and betaine function as zwitterions and only their carboxy groups participate in co-ordination.

In complex **1** (or **2**) every pair of Cd atoms are simultaneously bridged by two azide groups (or two isocyanate groups in **2**) in the end-on mode and one carboxy group of betaine in the *syn-syn* mode leading to a chain-like, one-dimensional polymer running parallel to the *c* axis (see Fig. 1). Both crystallographically independent Cd atoms occupy special positions in the unit cell: Cd(1) is located at an inversion centre in Wyckoff position 4(*a*), whereas Cd(2) lies on a 2 axis in Wyckoff position 4(*e*). The co-ordination geometry about Cd(1) is an irregular CdN_4O_2 octahedron with the most distorted angle at *ca.* 82.7(1)°, in which the carboxy oxygen atoms from two betaines

Table 1 Crystallographic data for complexes **1**–**4**

	1	**2**	**3**	**4**
Formula	$[Cd_2L^1{}_2(N_3)_4]$	$[Cd_2L^1{}_2(NCO)_4]$	$[Cd_3L^1{}_4(SCN)_6(H_2O)_2]$	$[CdL^2(NCS)_2]$
M	627.26	627.22	1190.40	359.76
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	*C*2/*c*	*C*2/*c*	*P*$\bar{1}$	*P*$\bar{1}$
Crystal size/mm	0.14 × 0.18 × 0.32	0.24 × 0.30 × 0.34	0.28 × 0.30 × 0.40	0.20 × 0.24 × 0.40
a/Å	20.748(8)	20.727(2)	9.419(2)	7.5633(9)
b/Å	9.417(4)	9.382(1)	9.930(2)	8.759(2)
c/Å	13.112(3)	13.003(1)	13.671(3)	10.237(3)
α/°	90	90	98.28(2)	82.09(2)
β/°	121.66(3)	120.74(1)	91.33(2)	75.31(2)
γ/°	90	90	117.40(1)	87.52(1)
U/Å^3	2180.8(3)	2173.8(3)	1117.6(4)	649.7(4)
Z	4	4	1	2
D_c/g cm^{-3}	1.91	1.92	1.77	1.84
D_m/g cm^{-3}	1.92	1.89	1.79	1.83
F(000)	1232	1232	594	356
μ/cm^{-1}	19.9	20.0	17.4	19.7
Transmission coefficients	0.57–0.62	0.85–0.97	0.66–0.78	0.52–0.58
2θ range/°	3–55	3–60	3–60	3–58
No. of data collected	2492	2665	5881	3027
No. of data used [$I > 3\sigma(I)$], *n*	2038	2125	4689	2548
No. of variables, *p*	139	139	257	145
R	0.026	0.028	0.037	0.033
R'	0.028	0.032	0.047	0.043
S	1.46	1.73	1.72	1.91

$R = \Sigma\Delta/\Sigma|F_o|$, $R' = [\Sigma w\Delta^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ and $S = [w\Delta^2/(n-p)]^{\frac{1}{2}}$ where $w = [\sigma^2(F_o) + K|F_o|^2]^{-1}$, $\Delta = ||F_o| - |F_c||$; $10^4K = 1, 3, 3$ and 2 for complexes **1**, **2**, **3** and **4** respectively. For **2**, extinction parameter $\chi = 0.002\,10(7)$ where $F_{corr} = F_c(1 + 0.002\chi F_c{}^2/\sin 2\theta)^{\frac{1}{4}}$.

Table 2 Atomic coordinates (× 10^5 for Cd, × 10^4 for other atoms) for complexes **1** and **2**

	1			**2**		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Cd(1)	0	0	0	0	0	0
Cd(2)	0	11 462(3)	25 000	0	10 835(3)	25 000
X(1)	851(2)	1 033(3)	4 571(2)	870(2)	933(3)	4 555(2)
X(2)	1 502(2)	719(3)	5 067(3)	1 511(2)	707(4)	5 071(3)
X(3)	2 134(2)	449(5)	5 546(3)	2 169(2)	488(5)	5 615(3)
X(4)	−646(2)	−525(3)	2 993(3)	−631(2)	−605(3)	3 005(2)
X(5)	−836(2)	−1 692(4)	2 671(3)	−879(3)	−1 708(5)	2 683(3)
X(6)	−1 047(4)	−2 804(5)	2 347(4)	−1 163(4)	−2 827(5)	2 333(4)
O(11)	−675(2)	2 817(3)	2 783(2)	−677(2)	2 811(3)	2 759(2)
O(12)	−634(2)	2 188(3)	4 466(2)	−607(2)	2 205(3)	4 482(2)
C(11)	−838(2)	2 941(3)	3 575(3)	−833(2)	2 937(3)	3 566(3)
C(12)	−1 355(2)	4 209(4)	3 327(3)	−1 373(2)	4 168(4)	3 304(3)
N(11)	−1 581(2)	4 586(3)	4 204(3)	−1 572(2)	4 564(3)	4 229(2)
C(13)	−899(3)	4 995(5)	5 394(4)	−902(3)	5 041(5)	5 366(4)
C(14)	−2 097(3)	5 850(4)	3 720(4)	−2 119(3)	5 771(5)	3 725(5)
C(15)	−2 008(3)	3 396(5)	4 346(5)	−1 955(3)	3 355(5)	4 445(5)

For complex **1** X(*n*) represents N(*n*), for **2** X(1)–X(6) represent N(1), C(1), O(1), N(2), C(2) and O(2) respectively.

Table 3 Atomic coordinates (× 10^5 for Cd, × 10^4 for other atoms) for complex **3**

Atom	*x*	*y*	*z*
Cd(1)	50 000	0	50 000
Cd(2)	8 839(3)	29 272(3)	29 447(2)
S(1)	−2 064(1)	1 634(1)	2 105(1)
C(1)	−3 099(4)	618(4)	2 933(3)
N(1)	−3 884(4)	−96(4)	3 489(3)
S(2)	340(1)	57(1)	3 268(1)
C(2)	2 052(5)	417(4)	3 857(3)
N(2)	3 243(4)	625(4)	4 246(3)
S(3)	2 995(2)	2 520(3)	−203(1)
C(3)	2 695(5)	2 783(5)	949(3)
N(3)	2 496(5)	2 946(5)	1 779(3)
O(11)	−30(3)	3 282(3)	4 560(2)
O(12)	2 527(3)	3 904(3)	4 494(2)
C(11)	1 349(4)	3 720(4)	4 964(3)
C(12)	1 500(4)	4 007(4)	6 100(3)
N(11)	3 124(4)	4 584(3)	6 638(2)
C(13)	3 820(5)	3 502(5)	6 382(3)
C(14)	2 929(6)	4 705(6)	7 733(3)
C(15)	4 259(5)	6 154(4)	6 432(3)
O(21)	1 736(4)	5 479(3)	2 900(2)
O(22)	406(4)	4 877(3)	1 410(2)
C(21)	1 405(4)	5 778(4)	2 078(3)
C(22)	2 435(5)	7 489(4)	2 014(3)
N(21)	2 371(4)	7 964(3)	1 027(2)
C(23)	2 842(6)	7 063(6)	245(3)
C(24)	3 533(7)	9 633(5)	1 133(4)
C(25)	742(5)	7 745(6)	713(4)
O(1w)	2 956(3)	−2 520(3)	4 674(2)

occupy *trans*-axial positions and the nitrogen atoms from four azide groups (or isocyanate groups) are situated in equatorial sites. The Cd(2) atom exhibits a more distorted-octahedral CdN_4O_2 environment, the most distorted bond angle about the Cd(2) atom being 81.0(1)°, with the carboxy oxygen atoms in *cis* positions and the remaining co-ordination sites also occupied by four nitrogen atoms. The differences in bond lengths and angles between **1** and **2** are trivial, as seen in Table 5.

$[Cd_3L^1_4(SCN)_6(H_2O)_2]$ **3**. Complex **3** consists of Cd atoms in two chemically different environments (Fig. 2). Atom Cd(1) occupies an inversion centre and is surrounded by four coplanar nitrogen atoms of end-to-end bridging thiocyanates and two oxygen atoms of *trans* aqua ligands in a CdN_4O_2 octahedron. Atom Cd(2) is in a highly irregular octahedral environment [O(11)–Cd(2)–O(12) 54.4(1)°], being co-ordinated by one oxygen atom of a unidentate betaine, two oxygen atoms from a bidentate chelate betaine, one nitrogen atom of a terminal thiocyanate, and two sulfur atoms of end-to-end bridging thiocyanates. The distances between Cd(2) and the two carboxy oxygen atoms of the bidentate L^1 are slightly different [Δ(Cd–O) ≈0.04Å] while the C–O bonds have the same length [1.248(5) Å], so that the chelating mode is almost symmetrical. Bond lengths and angles in the complex are listed in Table 6.

Table 4 Atomic coordinates (× 10^4 for Cd, × 10^4 for other atoms) for complex **4**

Atom	*x*	*y*	*z*
Cd(1)	330(3)	20 022(3)	39 816(2)
S(1)	2 701(2)	4 126(1)	2 980(1)
C(1)	1 793(5)	5 602(4)	3 758(4)
N(1)	1 213(5)	6 667(4)	4 269(4)
S(2)	−3 016(2)	2 902(2)	310(1)
C(2)	−2 286(5)	2 662(4)	1 687(5)
N(2)	−1 780(6)	2 520(4)	2 628(5)
O(11)	2 354(3)	494(3)	2 586(3)
O(12)	1 990(3)	186(3)	4 812(3)
C(11)	2 889(4)	−30(4)	3 615(4)
C(12)	4 679(4)	−912(4)	3 485(4)
C(13)	5 326(4)	−1 462(4)	2 097(4)
N(11)	7 169(3)	−2 277(3)	1 851(3)
C(14)	7 577(6)	−2 769(7)	454(5)
C(15)	8 661(5)	−1 222(5)	1 896(5)
C(16)	7 167(6)	−3 658(5)	2 885(6)

The angle O–C–O [123.8(3)°] of the chelating L^1 ligand, similar to those in related complexes, is significantly smaller than that of the unidentate ligand [126.5(3)°] as a consequence of the constraint imposed by co-ordination to the Cd(2) atom. However, it is still larger than those of typical bidentate chelate acetate ligands (usual range ≈116–121°). This may be attributed to the inductive effect of the positively charged ammonium group.

As depicted in Fig. 2, the crystal structure of complex **3** features a one-dimensional polymeric chain constructed from the linkage of a centrosymmetrical puckered 16-membered $(\text{-N-C-S-Cd})_4$ rings. Each ring is composed of two Cd(1) and two Cd(2) atoms and four end-to-end bridging thiocyanates functioning in *anti* and skew modes. The relevant torsion angles are Cd(1)–N(2)···S(2)–Cd(2) −178.8 and Cd(1a)–N(1)···S(1)–Cd(2) 77.0°, assuming both thiocyanato groups N(1)–C(1)–S(1) and N(2)–C(2)–S(2) to be linear; the latter are in fact almost linear and the bond angles at the central atom are 176.8(4) and 177.7(4)°, respectively. The ring is folded such that the cadmium atoms fall at the corners of a parallelogram. The

Table 5 Bond lengths (Å) and angles (°) for complexes **1** and **2**

	1	**2**		**1**	**2**
Cd(1)–X(1)	2.328(4)	2.328(4)	Cd(1)–X(4)	2.295(3)	2.301(3)
Cd(2)–X(1)	2.339(3)	2.342(3)	Cd(2)–X(4)	2.366(4)	2.352(4)
Cd(1)–O(12)	2.345(3)	2.334(3)	Cd(1)–O(11)	2.263(3)	2.279(3)
X(1)–X(2)	1.190(5)	1.160(5)	X(2)–X(3)	1.145(5)	1.192(5)
X(4)–X(5)	1.169(5)	1.136(6)	X(5)–X(6)	1.28(6)	1.175(7)
O(12)–C(11)	1.255(6)	1.241(4)	O(11)–C(11)	1.235(4)	1.250(5)
C(11)–C(12)	1.523(5)	1.521(5)	N(11)–C(12)	1.494(7)	1.504(6)
N(11)–C(13)	1.506(5)	1.489(5)	N(11)–C(14)	1.501(5)	1.497(6)
N(11)–C(15)	1.499(7)	1.491(7)			
X(1)–Cd(1)–X(4)	82.7(1)	83.0(1)	X(1)–Cd(1)–O(12)	86.4(1)	88.1(1)
X(4)–Cd(1)–O(12)	87.0(1)	88.9(1)			
X(1)–Cd(2)–X(1b)	174.8(2)	173.1(1)	X(1)–Cd(2)–X(4)	81.0(1)	81.6(1)
X(1)–Cd(2)–X(4b)	95.5(1)	93.7(1)	X(4)–Cd(2)–X(4b)	96.6(2)	95.3(2)
X(1)–Cd(2)–O(11)	89.8(1)	92.7(1)	X(4)–Cd(2)–O(12)	86.0(1)	88.0(2)
O(11)–Cd(2)–X(1b)	93.8(1)	91.9(1)	O(12)–Cd(2)–X(4b)	174.4(1)	173.2(1)
O(11)–Cd(2)–O(11b)	91.9(2)	89.3(2)			
Cd(1)–X(1)–Cd(2)	95.4(1)	93.6(1)	Cd(1)–X(4)–Cd(2)	95.5(1)	94.1(1)
Cd(1)–X(1)–X(2)	123.5(3)	126.3(3)	Cd(1)–X(4)–X(5)	120.0(3)	122.3(3)
Cd(1)–O(12)–C(11)	130.3(3)	130.6(3)	Cd(2)–X(1)–X(2)	126.5(3)	131.1(3)
Cd(2)–X(4)–X(5)	131.2(4)	136.3(4)	Cd(1)–O(11)–C(11)	131.2(2)	129.3(2)
X(1)–X(2)–X(3)	178.4(4)	179.0(5)	X(4)–X(5)–X(6)	177.3(6)	177.5(6)
O(11)–C(11)–O(12)	128.4(4)	128.3(3)	O(11)–C(11)–C(12)	111.2(3)	111.1(3)
O(12)–C(11)–C(12)	120.4(4)	120.5(4)	C(11)–C(11)–N(11)	119.5(3)	118.7(3)
C(12)–C(11)–C(13)	110.7(4)	111.7(4)	C(12)–C(11)–C(14)	107.8(3)	107.0(3)
C(12)–C(11)–C(15)	111.3(3)	110.6(3)	C(13)–N(11)–C(14)	108.0(3)	108.7(3)
C(13)–N(11)–C(15)	110.9(3)	111.0(3)	C(14)–C(11)–C(15)	108.0(4)	107.5(4)

Symmetry transformations: (a) $-x, -y, -z$; (b) $-x, -y, -\frac{1}{2} - z$. Atom X defined in Table 2.

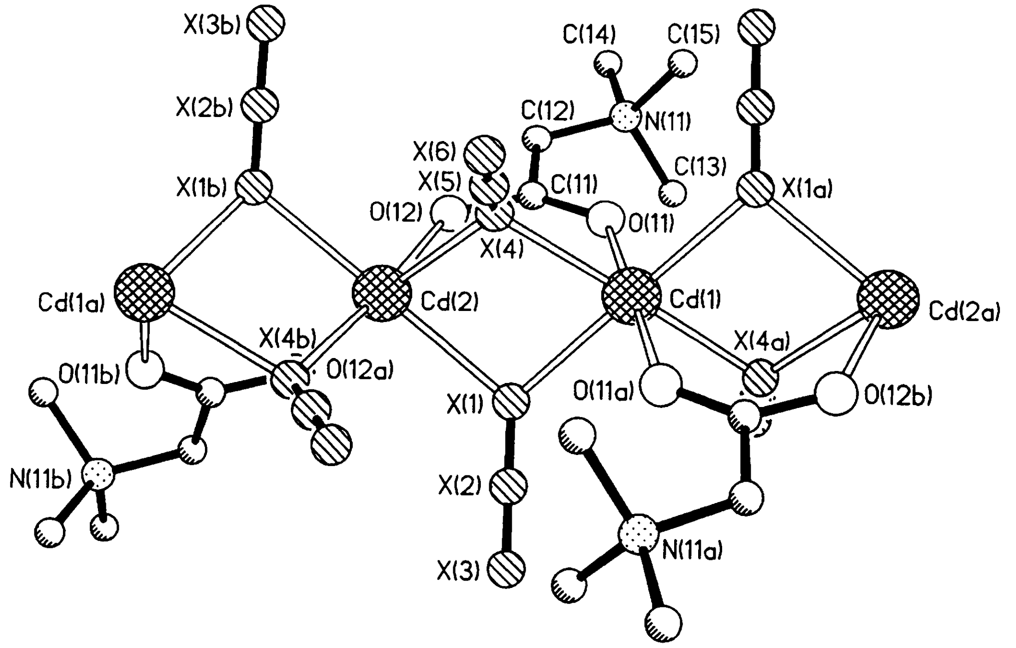


Fig. 1 Perspective view showing the co-ordination environment of the Cd(1) and Cd(2) atoms in $[Cd_2L^1{}_2(N_3)_4]$ **1** and $[Cd_2L^1{}_2(NCO)_4]$ **2** and the atom numbering scheme. Symmetric transformations are given in Table 5

adjacent puckered rings share common vertices at the Cd(1) atoms leading to an infinite chain running parallel to the *a* axis.

Each of the *trans*-related aqua ligands co-ordinated to Cd(1) forms donor hydrogen bonds with the carboxy oxygen atoms belonging to different L^1 ligands (see Fig. 2). The intrachain hydrogen bond, with an O $\cdots$ O distance of 2.776(6) Å between aqua ligand O(1wa) and carboxy oxygen atom O(11), pulls the bidentate chelate L^1 towards the bridging thiocyanate group S(1)–C(1)–N(1) and away from the terminal one N(3)–C(3)–S(3). The aqua ligand forms another hydrogen bond [O $\cdots$ O 2.744(6) Å] with the co-ordinated oxygen atom of the unidentate L^1 in an adjacent chain, thereby resulting in a two-dimensional network spread across the *ab* plane.

$[CdL^2(NCS)_2]$ **4**. Bond lengths and angles of the complex are listed in Table 7. As depicted in Fig. 3, each pair of cadmium atoms related by an inversion centre are alternately bridged by two μ-1,1 oxygen atoms of different L^2 ligands to form a four-membered $(\text{–O–Cd})_2$ ring, and by two μ-1,3 thiocyanate groups to form an eight-membered, chain-like $(\text{–N–C–S–Cd})_2$ ring. The torsion angle Cd(1)–S(1) $\cdots$ N(1)–Cd(1b) 56.0° [N(1)–C(1)–S(1) 177.4(3)°] is compatible to that of cyclohexane in the chair form (≈60°). The two different types of rings are

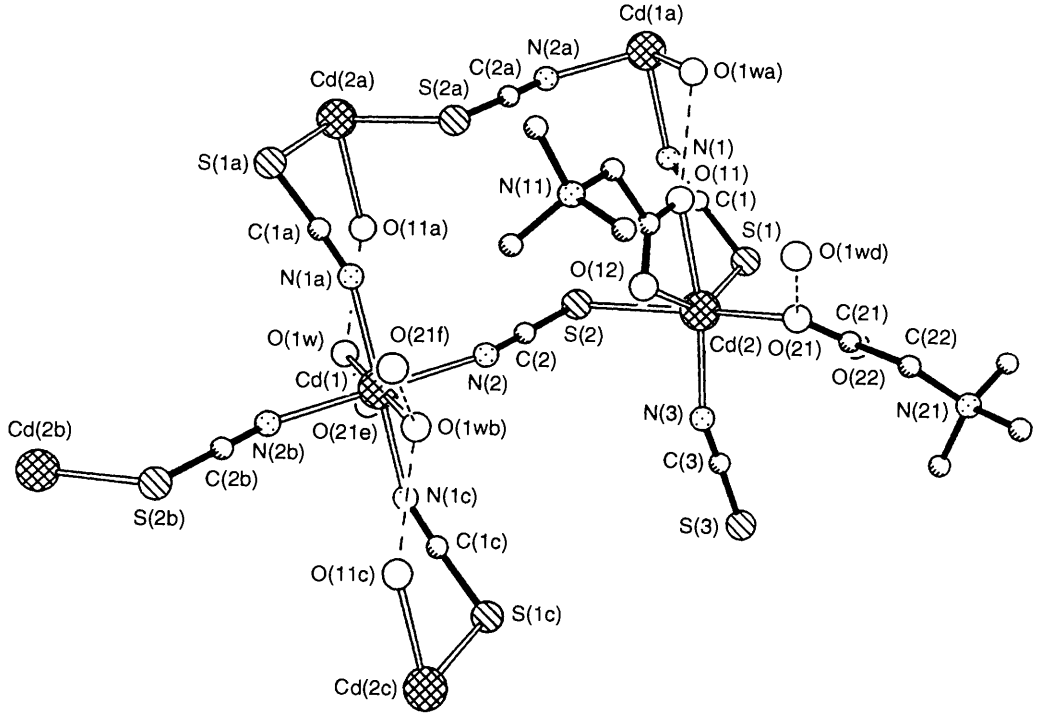


Fig. 2 Perspective view showing the co-ordination environment of the Cd(1) and Cd(2) atoms in $[Cd_3L^1_4(SCN)_6(H_2O)_2]$ **3** and the atom numbering scheme. Symmetry transformations are given in Table 6

Table 6 Bond lengths (Å) and angles (°) for complex **3**

Cd(1)–N(2)	2.289(5)	Cd(1)–N(1a)	2.349(4)	O(11)–C(11)	1.248(5)	O(12)–C(11)	1.248(5)
Cd(1)–O(1w)	2.318(2)			C(11)–C(12)	1.529(5)	C(12)–N(11)	1.493(5)
Cd(2)–S(1)	2.612(1)	Cd(2)–S(2)	2.759(1)	N(11)–C(13)	1.503(7)	N(11)–C(14)	1.507(5)
Cd(2)–N(3)	2.223(5)	Cd(2)–O(11)	2.426(3)	N(11)–C(15)	1.503(4)	O(21)–C(21)	1.271(5)
Cd(2)–O(12)	2.387(2)	Cd(2)–O(21)	2.289(3)	O(22)–C(21)	1.212(4)	C(21)–C(22)	1.538(5)
S(1)–C(1)	1.651(4)	C(1)–N(1)	1.151(5)	C(22)–N(21)	1.501(5)	N(21)–C(23)	1.501(7)
S(2)–C(2)	1.644(4)	C(2)–N(2)	1.145(6)	N(21)–C(24)	1.489(5)	N(21)–C(25)	1.490(7)
S(3)–C(3)	1.612(5)	C(3)–N(3)	1.156(6)				
O(1w)–Cd(1)–N(2)	86.3(1)	O(1w)–Cd(1)–N(1a)	96.0(1)	Cd(2)–O(12)–C(11)	91.7(2)	Cd(2)–O(21)–C(21)	115.6(2)
N(2)–Cd(1)–N(1a)	89.2(2)			S(1)–C(1)–N(1)	176.8(4)	S(2)–C(2)–N(2)	177.7(4)
S(1)–Cd(2)–N(3)	108.5(1)	S(1)–Cd(2)–O(11)	90.7(1)	S(3)–C(3)–N(4)	178.2(6)		
S(1)–Cd(2)–O(12)	144.8(1)	S(1)–Cd(2)–O(21)	102.3(1)	O(11)–C(11)–O(12)	123.8(3)	O(11)–C(11)–C(12)	114.7(3)
S(2)–Cd(2)–S(1)	88.0(1)	S(2)–Cd(2)–N(3)	92.1(1)	O(12)–C(11)–C(12)	121.5(3)	C(11)–C(12)–N(11)	118.0(3)
S(2)–Cd(2)–O(11)	87.5(1)	S(2)–Cd(2)–O(12)	86.0(1)	C(12)–N(11)–C(13)	112.4(3)	C(12)–N(11)–C(14)	107.3(3)
S(2)–Cd(2)–O(21)	169.2(1)	N(3)–Cd(2)–O(11)	160.8(1)	C(13)–N(11)–C(14)	107.6(4)	C(12)–N(11)–C(15)	110.7(3)
N(3)–Cd(2)–O(12)	106.4(1)	N(3)–Cd(2)–O(21)	87.8(2)	C(13)–N(11)–C(15)	109.9(3)	C(14)–N(11)–C(15)	108.8(3)
O(11)–Cd(2)–O(12)	54.4(1)	O(11)–Cd(2)–O(21)	89.0(1)	O(21)–C(21)–O(22)	126.5(3)	O(21)–C(21)–C(22)	111.5(3)
O(12)–Cd(2)–O(21)	83.6(1)			O(22)–C(21)–C(22)	122.0(4)	C(21)–C(22)–N(21)	117.4(3)
Cd(1a)–N(1)–C(1)	145.3(3)	Cd(1)–N(2)–C(2)	156.8(3)	C(22)–N(21)–C(23)	110.4(4)	C(22)–N(21)–C(24)	107.6(3)
Cd(2)–S(1)–C(1)	102.4(1)	Cd(2)–S(2)–C(2)	102.9(1)	C(23)–N(21)–C(24)	109.3(4)	C(22)–N(21)–C(25)	111.9(3)
Cd(2)–N(3)–C(3)	149.6(4)	Cd(2)–O(11)–C(11)	89.9(2)	C(23)–N(21)–C(25)	109.2(3)	C(24)–N(21)–C(25)	108.4(4)

Hydrogen bonding

O(11) ··· O(1wa)	2.776(6)	O(21) ··· O(1wd)	2.744(6)
Cd(1)–O(1w) ··· O(11a)	120.2(3)	Cd(1)–O(1w) ··· O(21e)	129.7(3)
Cd(2)–O(11) ··· O(1wa)	136.9(3)	Cd(2)–O(21) ··· O(1wd)	116.7(3)
O(21e) ··· O(1w) ··· O(11a)	96.7(3)		

Symmetry transformations: (a) $-x, -y, 1 - z$; (b) $1 - x, -y, 1 - z$; (c) $1 + x, y, z$; (d) $x, 1 + y, z$; (e) $x, -1 + y, z$; (f) $1 - x, 1 - y, 1 - z$.

linked alternately through the metal atoms to form polymeric chains extending along the *b* axis. Each Cd(1) atom displays an irregular octahedral co-ordination geometry, being surrounded by a chelating carboxy group, O(11) and O(12), a μ-1,1 carboxy O(12a) of ligand L^2, a terminal *N*-bound thiocyanate, and the N and S terminals of two end-to-end bridging thiocyanates. The bidentate carboxy group is folded out of the plane of the four-membered ring with a dihedral angle of 109.4(1)° along the shared O–Cd edge. The oxygen bridge is asymmetrical with the Cd(1)–O(12) and Cd(1a)–O(12) bond lengths at 2.346(3) and 2.486(2) Å, respectively.

The metal–oxygen bond lengths observed for complexes containing μ-*O*:*O*,*O′* carboxylate ligands are compared in Table 8. The combined monatomic bridged and bidentate chelate mode of ligand L^2 may be favoured by the large radius of the cadmium(II) ion, and the insertion of an additional methylene group between the anionic carboxy and the positively charged quaternary ammonium moieties reduces

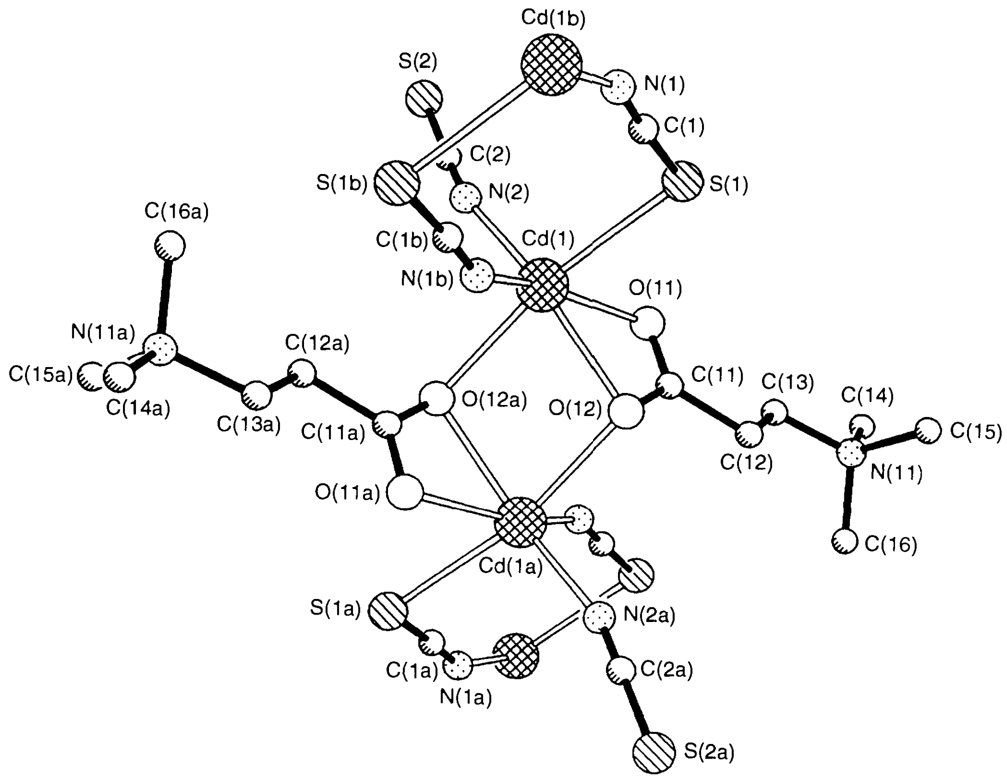


Fig. 3 Perspective view showing the co-ordination environment of the Cd(1) atom in $[CdL^2(NCS)_2]$ **4** and the atom numbering scheme. Symmetry transformations are given in Table 7

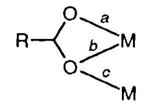
Table 7 Bond lengths (Å) and angles (°) for complex **4**

Cd(1)–S(1)	2.708(1)	Cd(1)–O(11)	2.432(3)
Cd(1)–O(12)	2.346(3)	Cd(1)–O(12a)	2.486(2)
Cd(1)–N(2)	2.178(5)	Cd(1)–N(1b)	2.253(4)
S(1)–C(1)	1.645(4)	S(2)–C(2)	1.624(5)
N(1)–C(1)	1.148(5)	N(2)–C(2)	1.113(7)
O(11)–C(11)	1.245(5)	O(12)–C(11)	1.277(4)
C(11)–C(12)	1.515(4)	C(12)–C(13)	1.519(5)
N(11)–C(13)	1.517(4)	N(11)–C(14)	1.503(6)
N(11)–C(15)	1.503(5)	N(11)–C(16)	1.493(5)
S(1)–Cd(1)–O(11)	79.4(1)	S(1)–Cd(1)–O(12)	93.4(1)
S(1)–Cd(1)–N(2)	103.2(1)	S(1)–Cd(1)–O(12a)	168.2(1)
S(1)–Cd(1)–N(1b)	90.8(1)	O(11)–Cd(1)–O(12)	54.9(1)
O(11)–Cd(1)–N(2)	99.5(1)	O(11)–Cd(1)–O(12a)	96.8(1)
O(11)–Cd(1)–N(1b)	156.5(1)	O(12)–Cd(1)–N(2)	146.6(1)
O(12)–Cd(1)–O(12a)	75.5(1)	O(12)–Cd(1)–N(1b)	105.1(1)
O(12a)–Cd(1)–N(1b)	88.4(1)	N(2)–Cd(1)–O(12a)	88.4(1)
N(2)–Cd(1)–N(1b)	103.5(1)		
Cd(1)–O(12)–Cd(1a)	104.5(1)	Cd(1)–S(1)–C(1)	101.3(1)
Cd(1)–N(2)–C(2)	160.6(4)	Cd(1)–O(11)–C(11)	89.5(2)
Cd(1)–O(12)–C(11)	92.7(2)	Cd(1a)–O(12)–C(11)	113.3(2)
Cd(1b)–N(1)–C(1)	156.2(3)		
S(1)–C(1)–N(1)	177.4(3)	S(2)–C(2)–N(2)	179.0(4)
O(11)–C(11)–O(12)	121.9(3)	O(11)–C(11)–C(12)	120.9(3)
O(12)–C(11)–C(12)	117.2(3)	C(11)–C(12)–C(13)	111.2(3)
N(11)–C(13)–C(12)	114.7(3)	C(13)–N(11)–C(14)	107.7(3)
C(13)–N(11)–C(15)	111.4(3)	C(13)–N(11)–C(16)	111.6(3)
C(14)–N(11)–C(15)	108.5(3)	C(14)–N(11)–C(16)	109.5(4)
C(15)–N(11)–C(16)	108.2(3)		

Symmetry transformations: (a) $-x$, $-y$, $1 - z$; (b) $-x$, $1 - y$, $1 - z$.

both the steric bulk about the co-ordination sphere and the inductive effect, resulting in a decrease in the O–C–O bond angle [O(11)–C(11)–O(12) 121.9(3)°]. Thus L^2 tends to form more bonds to cadmium as compared to L^1. It is noteworthy that **4** is the first cadmium–betaine complex found to exhibit the combined monatomic bridged and bidentate chelate mode which is uncommon among metal carboxylates.

Table 8 Metal–oxygen bond lengths (Å) in carboxylates exhibiting the combined monatomic bridging and bidentate chelating mode



Complex	*a*	*b*	*c*	Ref.
$[CdL^2(NCS)_2]$ **4**	2.432(3)	2.346(3)	2.486(2)	This work
$[\{Cd(HOC_6H_4CO_2)_2\cdot 2H_2O\}_2]$	2.314	2.535	2.271	32
$Cd(O_2CMe)_2\cdot 2H_2O$	2.294(4)	2.259(3)	2.297(4)	33
$[BaL^3{}_2(NCS)_2]$	2.862(3)	2.844(3)	2.724(3)	34
$[\{Hg_2(L^3{}_2)Cl_4\cdot HgCl_2\}_n]$	2.60(1)	2.59(1)	2.66(1)	14
$[\{Cd(Hsal)_2\cdot 2H_2O\}_2]$	2.325(4)	2.530(4)	2.291(4)	35
$[\{UO_2(NO_3)\}_2(sal)_2(Hdmap)_2]$	2.563(7)	2.467(7)	2.425(8)	36

H_2sal = Salicylic acid, dmap = 4-dimethylaminopyridine.

Infrared Spectroscopy.—The IR bands attributable to the betaine and pseudohalide ligands for complexes **1**–**4** are given in Table 9. All complexes show strong bands at *ca.* 1600 [$\nu_{asym}(CO_2)$] and 2100 cm^{-1} [ν_{asym}(pseudohalide)]. The difference between the asymmetric and symmetrical vibrations of a carboxylate group [$\Delta = \nu_{asym}(CO_2) - \nu_{sym}(CO_2)$] is commonly used to estimate its co-ordination mode to metal ions.[37] Significantly larger and smaller Δ values with respect to that of uncomplexed betaine (224 cm^{-1}) are indicative of the unidentate and chelate/bridging modes, respectively. In addition, the C–S stretching frequency can also be used to distinguish terminal *N*-bound or end-to-end bridging thiocyanate. Values of 804 and 805 cm^{-1} are expected for an *N*-bound thiocyanate group, while the smaller values 775 and 775 cm^{-1} are assigned to the end-to-end bridging mode due to weakening of the C–S bond.

Conclusion

The present study has shown that betaine and pseudohalide

Table 9 Infrared band assignments for the betaine and pseudohalide ligands in complexes **1**–**4**

	1	**2**	**3**	**4**	Uncomplexed betaine
$\nu_{asym}(CO_2)$	1608vs	1609vs	1654vs, 1595vs	1567vs, 1624vs	1624vs
$\nu_{sym}(CO_2)$	1401s	1402s	1397s	1432s	1388s
$\Delta(CO_2)$	207 (bridged)	207 (bridged)	198 (chelate) 257 (unidentate)		236
$\delta(CO_2)$	716m	722m	728m, 743m	709m	710m
$\nu_{asym}(N_3)$	2053vs, 2071vs				
$\nu_{asym}(NCO)$		2169vs (br) 2182vs (br) 2234vs			
ν(C–N)			2054vs, 2104vs	2065vs	
ν(C–S)			775w, 805w	775w, 804w	

Values are given in cm^{-1}; v = very, s = strong, m = medium, w = weak and br = broad. Note: $\Delta(CO_2)$ of bands of L^2 cannot be compared to those of L^1; they should be different for the uncomplexed compounds.

ligands exhibit various co-ordination modes in the cadmium(II) complexes **1**–**4**. All of the complexes have polymeric structures due to the versatile bridging abilities of the two kinds of ligands. It is notable that the carboxy group in **4** acts in the uncommon monatomic bridging plus bidentate chelating mode, which is rarely found among metal carboxylates. Hitherto, two other examples, namely $[BaL^3(NCS)_2]$[34] and $[\{Hg_2L^3{}_2Cl_2 \cdot HgCl_2\}_n]$[14] ($L^3$ = pyridinioacetate), have been found among the metal complexes of betaines.

There is no significant metal–metal interaction in complexes **1**–**4** although **1** and **2**, like $[Co_2L^1{}_2(N_3)_4]$ and $[Zn_2L^1{}_2(N_3)_4]$,[31] are all triply bridged with azide (or isothiocyanate) in the end-on mode and the carboxy group in the *syn-syn* mode which favours shortening of metal–metal distances. The metal–metal separations range from 3.209(1) to 3.451(2) Å in these four complexes, significantly larger than that in metallic cadmium (≈3.04 Å). The bridging azide (or isothiocyanate) and carboxy groups are almost symmetrically co-ordinated. It is interesting that the shorter Cd–N bonds are associated with the longer Cd–O bonds, or *vice versa*. This may be attributed to the electronic repulsion between the metal–ligand bonds or the conserved bond valence of the cadmium atom.

In the metal–betaine–azide complexes all azide ligands bridge in end-on mode so that the two end nitrogen atoms are somewhat different. In accordance with simple bonding theory, the N–N bond lengths between the co-ordinated and middle nitrogen atoms are expected to be slightly longer than those between the remote and the middle nitrogens,[38] as confirmed by the geometrical data of **1** in Table 5, as well as those of $[Co_2L^1{}_2(N_3)_4]$ and $[Zn_2L^1{}_2(N_3)_4]$.[31]

According to the Pearson acid–base theory, a thiocyanate ligand co-ordinated through nitrogen represents a hard base, whereas a sulfur-co-ordinated thiocyanate group is considered as a soft base. Therefore, thiocyanate is expected to co-ordinate *via* its sulfur atom to Cd^{II} which Pearson assigned to the group of soft acids due to its large ionic radius and low oxidation state. However, in numerous thiocyanato complexes cadmium does not always bind to thiocyanate *via* sulfur. As in the case of **3** and **4**, cadmium seems to prefer *N*-bonded thiocyanate, which may result from a higher negative charge on the nitrogen atom.

Finally, the unusually large O–C–O bond angles, especially in the *syn-syn* bridged mode, of the carboxy groups of the betaines, mainly caused by the inductive effect of the positively charged quaternary ammonium group, are a special feature of betaine ligands as compared to common monocarboxylates. The average O–C–O angles of betaines generally vary in this order: *syn-syn* bridged (≈128) > unidentate (≈126) > bidentate chelate (≈123°). Therefore, it may be concluded that chelating and bridging betaines always have larger O–C–O bond angles (by *ca.* 3°) than those in typical carboxylates (*syn-syn* bridging mode ≈125, bidentate chelate mode ≈120°).

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